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# Synthesis, crystal structure and characterization of the heterometallic tetranuclear butterfly cluster $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

Aapo U. Härkönen<sup>a</sup>, Markku Ahlgrén<sup>a</sup>, Tapani A. Pakkanen<sup>a,\*</sup>, Jouni Pursiainen<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Joensuu, PO Box 111, FIN-80101 Joensuu, Finland

<sup>b</sup> Department of Chemistry, University of Oulu, Linnanmaa, PO Box 333, FIN-90571 Oulu, Finland

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## Abstract

A new iridium–ruthenium mixed-metal cluster  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  has been synthesized and its structure has been determined by single-crystal X-ray diffraction.  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  shows a butterfly arrangement of metal atoms; with three terminal carbonyls on each metal atom and with the hydride ligands at Ru–Ru edges.

**Keywords:** Ruthenium; Iridium; Cluster; Carbonyl; Crystal structure; Heterometallic cluster

## 1. Introduction

Although there have been a number of studies of mixed-metal clusters (see for example Ref. [1]), only a few compounds containing a ruthenium and iridium mixed-metal framework are known. Structural information is available for an anionic cluster,  $[\text{RuIr}_3(\text{CO})_{12}]^-$  [2] and for a phosphine complex of the  $\text{Ru}_3\text{Ir}$  frame,  $[\text{Ru}_3\text{IrH}_2(\text{CO})_8(\text{PPh}_3)(\mu\text{-PPh}_2)(\text{PPhC}_6\text{H}_4)]$  [3].

Butterfly structures are found in many tetranuclear clusters with a wide variety of bridging ligands. Among the more extensively studied compounds are those containing a main-group atom such as carbon [4], nitrogen [5], oxygen [6], sulfur [7], and chlorine [8] in the bridging position. Typically, tetranuclear Fe [9] and Ru [10] clusters are known to form butterfly structures including mixed-metal butterfly compounds such as  $[\text{Ru}_3\text{CoH}(\text{CO})_{12}(\text{SMe}_2)]$  [7],  $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}_4(\text{CO})_9]$  [11] and  $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{CO})_{10}\text{BH}_2]$  [11]. The 64-electron cluster  $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}(\text{CO})_{10}\text{BH}_2]$  has been characterized structurally and spectroscopically. Its cluster core can be described either as an open-butterfly or a spiked triangle which is supported by a  $\mu_4$ -boron atom. Additionally, a neutral 60-electron butterfly cluster  $[\text{Ru}_3\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\text{H}_4(\text{CO})_9]$  has been

characterized spectroscopically. We report here the synthesis and X-ray crystal structure of a new chloride-bridged butterfly cluster containing ruthenium and iridium.

## 2. Results and discussion

### 2.1. Synthesis and structure of $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

$\text{Na}[\text{Ru}_3\text{H}(\text{CO})_{11}]$  and  $[\text{Ir}(\text{CO})_3\text{Cl}]_n$  were allowed to react in tetrahydrofuran (thf) for 2 h yielding 22% of the title compound.

The crystal structure of  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  possesses a butterfly arrangement of four metal atoms with the chloride bridging the two ruthenium ‘wings’. The iridium atom is located on the hinge bond of the butterfly structure. The structure is presented in Fig. 1, the atomic coordinates are shown in Table 1, bond distances in Table 2, and selected bond angles in Table 3.

The structure of  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  has a crystallographic mirror plane passing through the chloride ligand, the Ru(1) and Ir atoms. The Ru(2)–Cl–Ru(2a) bridge angle ( $94.5^\circ$ ) is more obtuse-angled than corresponding angles in other halogen-bridged compounds. For example, the metal–halogen–metal bond angles are  $88.3^\circ$  for  $[\text{PPN}][\text{Ru}_4(\text{CO})_{13}\text{Cl}]$  [8] and  $87.9^\circ$  for  $[\text{Os}_4\text{H}_3(\text{CO})_{12}\text{I}]$  [12]. In the structure of  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  the observed widening of the metal–halo-

\* Corresponding author.

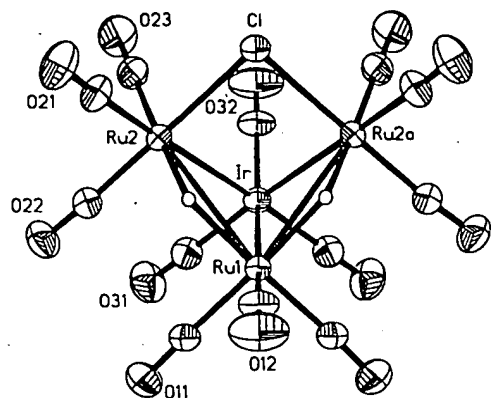


Fig. 1. Thermal ellipsoid labeling diagram for  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ . The thermal ellipsoids are drawn at the 40% probability level.

gen-metal bond angles may be a consequence of hydrogen-bridged bonds at the wing edges.

The cluster structure is comparable with butterfly structures of  $[\text{Ru}_4\text{H}_2(\text{CO})_{12}(\text{SMe}_2)]$  [7] and mixed-metal  $[\text{Ru}_3\text{CoH}(\text{CO})_{12}(\text{SMe}_2)]$  [7]. The structure of the  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  is a wing-tip-bridged butterfly cluster with dihedral angle of  $89.3^\circ$ . Corresponding values for the dihedral angles for  $\text{Ru}_4$  and  $\text{Ru}_3\text{Co}$  clusters are  $94.8^\circ$  and  $96.1^\circ$  respectively. Although the dihedral angle of  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$  is smaller than the corresponding similar angles of  $\text{Ru}_4$  and  $\text{Ru}_3\text{Co}$  clusters, these values are typical for wing-tip-bridged 62-electron butterfly clusters [13]. Each metal atom bears three terminal carbonyl ligands. The wing Ru–Ir bond distance of  $2.789(6)$  Å and the hinge Ru–Ru bond distance

Table 2  
Selected bond lengths (Å) for  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

Ir–Ru(1)	2.729(1)	Ru(2)–C(23)	1.905(7)
Ir–Ru(2)	2.789(1)	Ru(1)–H	1.770(6)
Ru(1)–Ru(2)	2.989(1)	Ru(2)–H	1.680(6)
Cl–Ru(2)	2.431(1)	O(11)–C(11)	1.121(8)
Ir–C(31)	1.914(7)	O(12)–C(12)	1.161(1)
Ir–C(32)	1.877(9)	C(21)–O(21)	1.096(9)
Ru(1)–C(11)	1.907(7)	C(22)–O(22)	1.130(8)
Ru(1)–C(12)	1.924(9)	C(23)–O(23)	1.136(8)
Ru(2)–C(21)	1.968(7)	O(31)–C(31)	1.124(9)
Ru(2)–C(22)	1.874(7)	O(32)–C(32)	1.146(1)

of  $2.729(8)$  Å are nearly equal in  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$ , but the wing Ru–Ru bond distances of  $2.989(7)$  Å are clearly longer than the remaining bonds, which implies hydrogen-bridged bonds [14]. The wing bond distances of Ru–Ir are clearly shorter than in the  $\text{Ru}_4$  ( $2.852(3)$  Å) and  $\text{Ru}_3\text{Co}$  ( $2.872(2)$  Å) butterfly clusters, but the Ru–Ir hinge bond distance is a little longer than the corresponding bonds in  $\text{Ru}_3\text{Co}$  ( $2.651(2)$  Å) cluster but a little shorter than  $\text{Ru}_4$  ( $2.875(2)$  Å) cluster [7].

After anisotropic refinement ( $R = 0.042$ ), the hydride ligands were found using Fourier difference calculations. The bridging hydride ligands lengthen metal-metal bonds and have a repulsive effect on the carbonyl groups. The hydride-bridged Ru(1)–Ru(2) bond of  $2.989$  Å is longer than the hinge bond Ir–Ru(1) of  $2.759$  Å and the wing Ru–Ru bond of  $2.789$  Å (Table 2). The bond angles Ru(2)/Ru(2a)–Ru(1)–C(12) are  $114.5(2)^\circ$ , whereas in  $[\text{Ru}_4\text{H}_2(\text{CO})_{12}(\text{SMe}_2)]$  and  $[\text{Ru}_3\text{CoH}-$

Table 1  
Atomic coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ ) for  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

Atom	x	y	z	$U^a$
Ir	3783(1)	2500	1941(1)	33(1)
Ru(1)	29(1)	2500	–80(1)	30(1)
Ru(2)	1512(1)	3600(1)	2874(1)	33(1)
Cl	1019(3)	2500	4573(3)	42(1)
O(11)	557(12)	3811(4)	–2353(8)	73(2)
O(12)	–4346(11)	2500	–1850(10)	73(3)
O(21)	–1629(9)	4521(4)	3627(8)	69(2)
O(22)	2169(9)	4996(3)	878(7)	62(2)
O(23)	4873(10)	4171(4)	5875(8)	81(2)
O(31)	5148(11)	3892(5)	314(10)	79(2)
O(32)	6974(12)	2500	5287(11)	93(4)
C(11)	396(10)	3334(4)	–1481(7)	45(1)
C(12)	–2703(13)	2500	–1154(10)	44(2)
C(21)	–491(11)	4206(4)	3353(9)	48(1)
C(22)	1918(10)	4458(4)	1597(8)	43(1)
C(23)	3625(11)	3953(5)	4752(9)	52(2)
C(31)	4617(10)	3381(5)	905(9)	49(2)
C(32)	5713(14)	2500	4049(12)	53(2)
H	–348(9)	3246(4)	1256(7)	28(2)

<sup>a</sup> Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U$  tensor.

Table 3  
Selected bond angles (deg) for  $[\text{Ru}_3\text{IrH}_2(\text{CO})_{12}\text{Cl}]$

C(32)–Ir–C(31)	100.9(3)	Ru(2a)–Ru(1)–H	87(2)
C(31)–Ir–C(31a)	96.7(4)	Ru(2a)–Cl–Ru(2)	94.5(1)
C(32)–Ir–Ru(1)	151.5(3)	O(12)–C(12)–Ru(1)	177.9(8)
C(31)–Ir–Ru(1)	97.9(2)	O(11)–C(11)–Ru(1)	177.4(7)
C(32)–Ir–Ru(2)	93.1(2)	O(31)–C(31)–Ir	178.4(7)
C(31)–Ir–Ru(2)	90.0(2)	O(32)–C(32)–Ir	175.6(1)
C(31a)–Ir–Ru(2)	163.0(2)	C(22)–Ru(2)–C(23)	91.0(3)
C(11)–Ru(1)–C(11a)	90.5(4)	C(22)–Ru(2)–C(21)	93.3(3)
C(11)–Ru(1)–C(12)	93.9(3)	C(23)–Ru(2)–C(21)	97.6(3)
C(11)–Ru(1)–Ir	93.1(2)	C(22)–Ru(2)–Cl	179.0(2)
C(12)–Ru(1)–Ir	170.0(2)	C(23)–Ru(2)–Cl	88.0(2)
C(11)–Ru(1)–Ru(2)	91.7(2)	C(21)–Ru(2)–Cl	86.5(2)
C(11a)–Ru(1)–Ru(2)	151.3(2)	C(22)–Ru(2)–Ir	93.1(2)
C(12)–Ru(1)–Ru(2)	114.5(2)	C(23)–Ru(2)–Ir	91.9(3)
C(11)–Ru(1)–H	92(2)	C(21)–Ru(2)–Ir	168.4(2)
C(11a)–Ru(1)–H	178(2)	Cl–Ru(2)–Ir	87.3(1)
C(12)–Ru(1)–H	86(2)	C(22)–Ru(2)–Ru(1)	91.5(2)
Ir–Ru(1)–H	87(2)	C(23)–Ru(2)–Ru(1)	148.1(3)
Ru(2)–Ru(1)–H	29(2)	C(21)–Ru(2)–Ru(1)	113.9(2)
C(22)–Ru(2)–H	91(2)	Cl–Ru(2)–Ru(1)	89.5(1)
C(23)–Ru(2)–H	177(2)	Cl–Ru(2)–H	90(2)
C(21)–Ru(2)–H	83(2)	O(22)–C(22)–Ru(2)	177.2(6)
Ir–Ru(2)–H	87(2)	O(21)–C(21)–Ru(2)	177.8(7)
Ru(1)–Ru(2)–H	31(2)	O(23)–C(23)–Ru(2)	179.2(8)

(CO)<sub>12</sub>(SMe<sub>2</sub>) the corresponding angles for the hydride-bridged metal–metal edge are 109.5(4)° and 132.0(4)° respectively, and the non-bridged metal–metal edge angles are 84.9(4)° and 69.8(4)° respectively. In [Ru<sub>4</sub>H<sub>2</sub>(CO)<sub>12</sub>(SMe<sub>2</sub>)] one hydrogen-bridged bond is in the hinge position and the other in the wing side, as in [Ru<sub>3</sub>CoH(CO)<sub>12</sub>(SMe<sub>2</sub>)].

In CDCl<sub>3</sub> solution, the room-temperature <sup>1</sup>H NMR spectrum of [Ru<sub>3</sub>IrH<sub>2</sub>(CO)<sub>12</sub>Cl] exhibits one sharp hydride resonance at δ = 18.7 ppm. It can be assigned to the Ru(μ<sub>2</sub>-H)Ru bridging hydrogen atoms which are equivalent.

In future work the goal is to find ways to eliminate the chlorine ligand to give the neutral hydride butterfly cluster compound [Ru<sub>3</sub>IrH<sub>3</sub>(CO)<sub>12</sub>] and find synthetic methods to produce new ruthenium and iridium mixed-metal clusters, with either closed or open frames.

### 3. Experimental section

#### 3.1. General comments

All manipulations except chromatographic separations were carried out under a nitrogen atmosphere and with deoxygenated solvents. [Ir(CO)<sub>3</sub>Cl]<sub>n</sub> was of commercial origin (Strem). Na[Ru<sub>3</sub>H(CO)<sub>11</sub>] [15] was prepared by published methods.

Infrared spectra were recorded in *n*-hexane on a Nicolet 20SXC FT-IR spectrometer. The <sup>1</sup>H NMR spectra were measured on a Bruker AM-250 spectrometer with CDCl<sub>3</sub> as solvent at 273 K with Me<sub>4</sub>Si as reference. Crystals were grown by evaporation of the solvent from a saturated hexane–CH<sub>2</sub>Cl<sub>2</sub> solution.

#### 3.2. Synthesis of [Ru<sub>3</sub>IrH<sub>2</sub>(CO)<sub>12</sub>Cl]

The compound [Ir(CO)<sub>3</sub>Cl]<sub>n</sub> (37 mg, 0.118 mmol) was added to a solution of Na[Ru<sub>3</sub>H(CO)<sub>11</sub>] (134 mg, 0.211 mmol) in thf (50 ml). The solution was stirred at room-temperature for 2 h. The reddish-brown solution was filtered and evaporated in vacuo and the residue was extracted by hexane and CH<sub>2</sub>Cl<sub>2</sub>. Hexane extract showed CO-stretching vibrations characteristic for [Ru<sub>3</sub>(CO)<sub>12</sub>]. Dichloromethane extract was chromatographed with thin layer chromatography. Elution of CH<sub>2</sub>Cl<sub>2</sub> extract with a hexane–dichloromethane (5:1) mixture gave a yellow band that showed CO-stretching vibrations characteristic for [Ru<sub>3</sub>(CO)<sub>12</sub>] (27 mg). Further elution with a hexane–dichloromethane (5:1) mixture gave a reddish-brown fraction, which was dried in vacuo and recrystallized from hexane–dichloromethane at 4 °C. Air-stable dark red cubic crystals were formed; yield 23 mg (22%). IR: ν(CO) 2089 w, 2078 s, 2067 s, 2054 vs, 2035 w, 2023 m, 2006 w cm<sup>-1</sup>. <sup>1</sup>H NMR: –18.7 (s) ppm. A fraction that was not eluted by a

Table 4  
Crystallographic data for [Ru<sub>3</sub>IrH<sub>2</sub>(CO)<sub>12</sub>Cl]

Formula	C <sub>12</sub> H <sub>2</sub> ClIrO <sub>12</sub> Ru <sub>3</sub>
Formula weight	869.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /m
a(Å)	7.527(1)
b(Å)	16.233(3)
c(Å)	8.693(1)
β(deg)	111.42(1)
V(Å <sup>3</sup> )	988.8(3)
Z	2
D <sub>calc</sub> (g cm <sup>-3</sup> )	2.92
Crystal dimensions (mm <sup>3</sup> )	0.4 × 0.4 × 0.5
Radiation	Mo K α
Monochromator	graphite
2θ limits (deg)	5–65
No. of reflections measured	3921
No. of unique data	3702
No. of I > 2σ(I)	3195
μ(Mo K α) (cm <sup>-1</sup> )	95.0
R[I > 2σ(I)] <sup>a</sup>	0.042
wR(F <sup>2</sup> ) <sup>b</sup>	0.109
S (goodness of fit)	1.093

<sup>a</sup> R = Σ||F<sub>o</sub>| – |F<sub>c</sub>||/Σ|F<sub>o</sub>|.

<sup>b</sup> weight = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0498P)<sup>2</sup>] where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3.

hexane–dichloromethane (5:1) mixture remained. Attempts to crystallize this fraction failed.

#### 3.3. Crystallographic summary

Pertinent crystal and refinement data are listed in Table 4. Data were collected on a Nicolet R3m diffractometer using Mo K α radiation (λ = 0.71073 Å). Accurate cell parameters were obtained from 25 automatically centered reflections in the range 15 < 2θ < 35°. Intensities were corrected for background, polarization, and Lorentz factors. Empirical absorption corrections were made from ψ-scan data. Transmission factors being T<sub>min</sub> = 0.113 and T<sub>max</sub> = 0.178.

The metal atom positions were solved by direct methods using the SHELXTL program package [16]. All remaining non-hydrogen atoms were located by the usual combination of full-matrix least squares refinement and difference electron density syntheses using SHELXL93 [17]. Metal, oxygen, chlorine, and carbon atoms were anisotropically refined in the structure. Hydride ligands were located from a difference Fourier map but not refined.

A complete list of bond lengths and angles and tables of thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.

### References

- [1] R.D. Adams, in E.W. Abel, F.G.A. Stone and G. Wilkinson (eds.), *Comprehensive Organometallic Chemistry*, Vol. 10, Pergamon, Oxford, 1995, Chapter 1.

- [2] A. Fumagalli, F. Demartin and A. Sironi, *J. Organomet. Chem.*, 279 (1985) C33.
- [3] H. Jungbluth, G. Süss-Fink, M.A. Pellinghelli and A. Tiripicchio, *Organometallics*, 9 (1990) 1670.
- [4] J.S. Bradley, *Adv. Organomet. Chem.*, 22 (1985) 1.
- [5] W.L. Gladfelter, *Adv. Organomet. Chem.*, 24 (1985) 41.
- [6] C.K. Schauer and D.F. Shriver, *Angew. Chem. Int. Ed. Engl.*, 26 (1987) 255.
- [7] S. Rossi, J. Pursiainen and T.A. Pakkanen, *Organometallics*, 10 (1991) 1390.
- [8] G.R. Steinmetz, A.D. Harley and G.L. Geoffroy, *Inorg. Chem.*, 19 (1980) 2985.
- [9] M. Manassero, M. Sansoni and G.J. Longoni, *J. Chem. Soc. Chem. Commun.*, (1976) 919.
- [10] S. Rossi, J. Pursiainen and T.A. Pakkanen, *J. Organomet. Chem.*, 436 (1992) 55.
- [11] J.R. Galsworthy, C.E. Housecroft, D.M. Matthews, R. Ostrander and A.L. Rheingold, *J. Chem. Soc. Dalton Trans.*, (1994) 69.
- [12] B.F.G. Johnson, J. Lewis, P.R. Raithby, G.M. Sheldrick, K. Wong and M. McPartlin, *J. Chem. Soc. Dalton Trans.*, (1978) 673.
- [13] E. Sappa, A. Tiripicchio, J.C. Carty and G.E. Toogood (eds.), *Progress in Inorganic Chemistry*, Vol. 35, Wiley, New York, 1987, p. 437.
- [14] T.A. Pakkanen, J. Pursiainen, T. Venäläinen and T.T. Pakkanen, *J. Organomet. Chem.*, 372 (1989) 129.
- [15] B.F.G. Johnson, J. Lewis, P.R. Raithby and G. Süss, *J. Chem. Soc. Dalton Trans.*, (1978) 1356.
- [16] G.M. Sheldrick, *SHELXTL-PLUS*, Release 4.11/v, 1990, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA.
- [17] G.M. Sheldrick, *SHELXL93, Program for the refinement of crystal structures*, University of Göttingen, Germany, 1993.